OVERALL OBJECTIVE

Provide experimental source-term data and models that can be used to help predict the potential for release of radionuclides from a repository in the unlikely event that spent fuel is contacted by groundwater.
BACKGROUND

- Over 98% of the 1000-year radioactive inventory in spent fuel is Am and Pu.
  * Release will be controlled by solubility (or possibly colloidal transport).

- Release of soluble radionuclides ($^{99}$Tc, $^{135}$Cs, $^{129}$I) will be controlled by two separate mechanisms because of the heterogeneous nature of spent fuel.
  * Rapid release of Cs and I (0.1 to 20% of total inventories) from gap and grain boundaries.
  * Long-term release of soluble radionuclides contained within the UO$_2$ matrix of spent fuel will be controlled by the dissolution rate of that matrix.
PWR Spent Fuel Radionuclide Inventories at 1,000 Years

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half-Life (years)</th>
<th>1,000-Year Activity (% of Total)</th>
<th>Cumulative Activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}$Am</td>
<td>432</td>
<td>51.3</td>
<td>51.3</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>7,380</td>
<td>1.8</td>
<td>53.1</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>6,570</td>
<td>27.4</td>
<td>80.5</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>24,100</td>
<td>17.5</td>
<td>98.0</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>375,800</td>
<td>0.10</td>
<td>98.1</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
<td>88</td>
<td>0.06</td>
<td>98.1</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>213,000</td>
<td>0.75</td>
<td>98.9</td>
</tr>
<tr>
<td>$^{135}$Cs</td>
<td>2,300,000</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>15,700,000</td>
<td>0.0018</td>
<td></td>
</tr>
</tbody>
</table>
Soluble Fission-Product Release from UO₂ Fuel in Water Under Oxidizing Conditions

DATA NEEDS/MOTIVATION

- Thermodynamic data for key solid/solution reactions involving low-solubility radionuclides.
  
  * These radionuclides constitute most of the activity in spent fuel, and solubility will control their release unless colloids make an important contribution.

- Experiments to determine the nature and importance of actinide-bearing colloids.

- Gap inventories and grain-boundary inventories of soluble radionuclides.
  
  * YMP assumes immediate dissolution of gap and grain-boundary inventories upon contact by water--inventories must be measured.
DATA NEEDS/MOTIVATION (Continued)

- Demonstration that spent fuel matrix dissolves congruently.
  * YMP assumes matrix dissolution controls dissolution of soluble radionuclides--this needs verification.

- Kinetics of spent fuel matrix dissolution as a function of water chemistry and fuel condition.
  * Spent fuel dissolution mechanism is poorly understood.
  * The effect of prior oxidation on dissolution is unknown.
  * A better understanding of these factors is needed to predict the long-term release of soluble radionuclides.
ACCOMPLISHMENTS  FY 1987 - 1992

- Completed three series of semi-static spent fuel dissolution tests; the first in deionized water; the second and third in J-13 water.
  * Results are documented in HEDL-TME 84-30, PNL-7169 and PNL-7170

- Developed methods for:
  * Preparing separated fuel-grain specimens, thus exposing grain boundaries and allowing inventories of radionuclides concentrated therein to be measured.
  * Conducting flow-through dissolution-rate measurements.

- Measured gap and grain-boundary inventories of Cs, Tc, and Sr -- only two different fuels tested to date.

- Showed that spent fuel grains dissolve nearly congruently -- only three different fuels tested to date.

- Showed importance of Si and Ca in test solutions.
Summary of Results for Artificially Defected Cladding

- $^{137}$Cs concentrations 2 to 4 times lower from defected rods compared to bare fuel tests.
- $^{99}$Tc concentrations 20 to 40 times lower from defected rods compared to bare fuel tests.
- Actinide concentrations 100 to 1000 times lower from defected rods compared to bare fuel tests.
Annual Release Rates at 25°C in J-13 Water as Fraction of 1,000-Year Inventories

<table>
<thead>
<tr>
<th>Actinide</th>
<th>log(Release Rate)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>-8.6</td>
</tr>
<tr>
<td>Np</td>
<td>-8.8</td>
</tr>
<tr>
<td>Pu</td>
<td>-9.0</td>
</tr>
<tr>
<td>Am</td>
<td>-9.1</td>
</tr>
</tbody>
</table>

* Assumes water flow rate of 20 L/Yr per waste package containing 3140 kg of 33 MWd/kgM PWR fuel.
Cs Gap and Grain Boundary Inventories

![Graph showing the relationship between Fission Gas Release (%) and Inventories (%). The graph includes data points for both Gap and Grain Boundary inventories.](image-url)
Tc & Sr Gap and Grain Boundary Inventories

![Graph showing inventories of Tc and Sr gap and grain boundary as a function of fission gas release.](image)

- **Tc Gap** represented by **O**
- **Tc Grain Boundary** represented by **●**
- **Sr Gap** represented by **△**
- **Sr Grain Boundary** represented by **▲**

The graph plots inventories (%) on the y-axis against fission gas release (%) on the x-axis.
Spent Fuel Dissolution Testing

Radiochemical Analyses:
- U by Laser Fluorimetry
- $^{39}$Cs by Direct Gamma Counting
- $^{99}$Tc and $^{89}$Sr by Chemical Separation Followed by Beta Counting
Dissolution Rate of Fuel Grains

20 mM Carbonate, pH = 8, 25°C

Fraction per Day ($x 10^4$)

Time (days)

Normalized Rate (mg/m$^2$/day)
Flow Rate Data for Fuel Grains

20 mM Carbonate, pH = 8, 25°C
Flow-Through Test with UO₂
0.2 mL/min, 25°C

U Conc. (ng/mL)

J-13 Water
NaHCO₃
NaHCO₃ + Ca + Si
NaHCO₃ + Ca

Time (Days)

0 10 20 30 40 50 60 70
ACCOMPLISHMENTS '87 - '92 (Continued)

- Developed dissolution test matrix (UO₂ at LLNL; spent fuel at PNL) to investigate:
  * temperature (25 to 75°C)
  * carbonate/bicarbonate concentration (2 x 10⁻⁴ to 2 x 10⁻² M)
  * pH (8 to 10)
  * oxygen fugacity (20% to 0.2%)
U Dissolution Rate
20 mM NaHCO$_3$, pH = 8

![Graph showing U Dissolution Rate over time for Spent Fuel and UO$_2$. The y-axis represents U Normalized Rate (mg/m$^2$/day), and the x-axis represents Time (days).]
For a limited number of fuels and test conditions, showed that dissolution rates of unirradiated UO$_2$ and spent fuel up to burnup of 50 MWd/kgM are roughly equal.

For one fuel and one test condition, showed that dissolution rates of spent fuel oxidized to U$_{4}O_{9+x}$ (UO$_2.4$) are roughly equal to those of unoxidized fuel.

For one test condition, showed that dissolution rates of unirradiated UO$_2$ and U$_3$O$_7$ are roughly equal.

For one test condition, showed that dissolution rates of unirradiated U$_3$O$_8$ are much higher than UO$_2$.

For one fuel and one test condition, demonstrated that flow-through fractional dissolution rates are not substantially different from those in semi-static tests.
Spent Fuel Dissolution Rates

2 mM NaHCO₃/Na₂CO₃, pH = 9, 50°C

<table>
<thead>
<tr>
<th>25</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>

Normalized Rate (mg/m²/day)

Time (Days)

Grains
- U-Ox
- U-Unox
- Cs-Ox
- Cs-Unox

Particles
Dissolution Rate of Unirradiated Specimens

20 mM NaHCO₃, pH = 8

- U₃O₈
- U₃O₇
- UO₂
Dissolution Rate of Unirradiated Specimens

0.2 mM Na$_2$CO$_3$, 0.2% Oxygen, pH = 10

Normalized Rate (mg/m$^2$/day)

Time (days)
Spent Fuel Dissolution Rates
J-13 Water, 25°C

Semi-Static

U  6.1 x 10^{-7}

\(^{137}\)Cs  6.9 x 10^{-7}

\(^{99}\)Tc  3.9 x 10^{-7}

\(^{90}\)Sr
SUMMARY OF ACCOMPLISHMENTS

- Showed that solubility constraints are likely to limit release of actinides (over 98% of total activity) to far less than 1 part in 100,000 per year unless colloids make an important contribution.

- Developed method for measuring grain-boundary inventories and showed, for the two fuels tested, that the inventories of Cs, Sr, and Tc are quite small.

- Developed method for measuring the dissolution rate of the UO₂ matrix in spent fuel and demonstrated (only 3 fuels) that it dissolves congruently.

- For a very limited number of fuels and test conditions, showed that oxidation (up to UO₂,₄ and U₃O₇) and burnup (unirradiated up to 50 MWd/kgM) have little effect on dissolution rates under the conditions tested.
SUMMARY OF ACCOMPLISHMENTS (Continued)

- For a single fuel and test condition, showed that dissolution rates in flow-through tests are not substantially different from those observed in semi-static (more repository relevant) tests.
- Showed that the presence of Si or Ca in test solutions has an important influence on dissolution rates.
- Embarked on systematic test program to determine the effects of various parameters on the dissolution rate of the UO₂ matrix of spent fuel.
GOALS FOR FY-1993 AND BEYOND

1) Generate thermodynamic data for key solid/solution reactions involving low-solubility radionuclides.

2) Work to identify solid phases that control the solubilities of the actinides under expected repository conditions.

3) Develop experiments to determine the nature and importance of actinide-bearing colloids.
GOALS (Continued)

4) Gap and grain-boundary inventory measurements.
   - Extend measurements to a variety of fuels to correlate inventories with other fuel parameters such as burnup and fission gas release.

5) Flow-through dissolution-rate measurements.
   - Measure dissolution rates for spent fuel oxidized beyond UO$_2$.
   - Measure dissolution rates for oxidized spent fuel under other water chemistry test conditions. Also test additional oxidized fuels.
   - Complete current test matrix with UO$_2$ and spent fuel.
   - Expand test matrix to include Si, Ca, and waste package corrosion products.
   - Extend measurements to gadolinia fuels and fuels with very high burnup.
PUBLICATIONS


C. N. Wilson, Results from NNWSI Series 2 Bare Fuel Dissolution Tests, PNL-7169, Pacific Northwest Laboratory, Richland, WA, 1990.

C. N. Wilson, Results from NNWSI Series 3 Spent Fuel Dissolution Tests, PNL-7170, Pacific Northwest Laboratory, Richland, WA, 1990.


